# Isocyano Compounds Newly Recognized in Photochemical Reaction of Thiazole: Matrix-isolation FT-IR and Theoretical Study

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***Table S1.*** *Observed and calculated wavenumbers, and IR intensities of thiazole (**1**) isolated in solid argon matrices.*

| Observed | | Ar matrix[a] | $N_2$ matrix[a] | Calculated[b] | | Assignment[d] |
|---|---|---|---|---|---|---|
| ν / cm$^{-1}$ | Intensity[c] | ν / cm$^{-1}$ | ν / cm$^{-1}$ | ν / cm$^{-1}$ | Intensity / km mol$^{-1}$ | |
| 603.9 | 2.9 | 604 | 607 | 600.71 | 1.44 | Ring deform |
| 610.5 | 2.7 | | | 608.70 | 16.70 | Ring deform |
| 714.1 | 8.3 | 717 | 721 | 721.58 | 22.64 | C−H deform |
| 717.2 | 30.1 | | | | | |
| 727.1 | 12.6 | 727 | 726 | 729.86 | 0.12 | Ring deform |
| 795.6 | 100.0 | 796 | 805/807 | 797.50 | 45.02 | C−H deform |
| 862.4 | 98.0 | 862/863 | 865/869 | 844.82 | 48.70 | Breathing |
| 863.3 | 43.8 | | | | | |
| 877.5 | 9.1 | 878 | 880/881 | 868.11 | 6.42 | Ring deform |
| 878.3 | 6.3 | | | | | |
| 887.7 | 1.1 | vw | | 901.28 | 0.60 | C−H deform |
| 1042.7 | 15.3 | 1043/1044 | 1042/1045 | 1044.44 | 7.07 | C−H bending |
| 1043.9 | 13.4 | | | | | |
| 1123.4 | 3.7 | 1124/1126 | 1123/1124 | 1127.99 | 5.27 | C−H bending |
| 1123.9 | 4.4 | | | | | |
| 1124.6 | 4.3 | | | | | |
| 1240.1 | 35.5 | 1240 | 1240/1244 | 1238.86 | 11.97 | C−H bending |
| 1320.4 | 3.9 | 1323/1325 | 1321/1323 | 1328.31 | 3.39 | Ring stretching |
| 1323.3 | 10.7 | | | | | |
| 1324.5 | 13.0 | | | | | |
| 1325.2 | 17.0 | | | | | |
| 1382.8 | 15.9 | 1382/1386 | 1383/1382 | 1399.88 | 24.02 | Ring stretching |
| 1385.5 | 24.1 | | | | | |
| 1386.4 | 13.7 | | | | | |
| 1483.1 | 16.5 | 1483/1484 | 1484 | 1494.06 | 26.22 | Ring stretching |
| 1484.0 | 16.1 | | | | | |
| 1484.5 | 19.7 | | | | | |
| 1488.2 | 10.5 | | | | | |
| 3091.9 | 2.2 | 3092 | 3101 | 3085.43 | 3.33 | C−H stretching |
| 3097.2 | 1.3 | vw | vw | 3091.22 | 0.02 | C−H stretching |
| 3100.8 | 1.0 | | | | | |
| 3144.0 | 3.1 | 3144 | 3139 | 3128.79 | 0.96 | C−H stretching |
| 3145.0 | 2.9 | | | | | |

[a]Reported in the reference of "Halasa, A.; Reva, I.; Lapinski, L.; Nowak, M. J.; Fausto, R. Conformational Changes in Thiazole-2-Carboxylic Acid Selectively Induced by Excitation with Narrowband Near-IR and UV Light. *J. Phys. Chem. A* **2016**, 120, 2078–2088". [b]Calculated at the UB3LYP/aug-cc-pVTZ level. Scaling factors of 0.96 and 0.98 are applied to the regions over 2800 cm$^{-1}$ and below 1900 cm$^{-1}$, respectively. [c]Relative intensity is normalized to the most intense band. [d]Reported in the reference of "Sbrana, G.; Castellucci, E.; Ginanneschi, M. Infra-Red and Raman Spectra of Five-Membered Heterocyclic Molecules—Oxazole and Thiazole. *Spectrochim. Acta A* **1967**, 23, 751–758".

***Table S2.*** *Calculated wavenumbers and IR intensities of 2-isocyanoethenethiol (**2**).*[a]

| *syn*-(*Z*)-**2** | | *anti*-(*Z*)-**2** | | *syn*-(*E*)-**2** | | *anti*-(*E*)-**2** | |
|---|---|---|---|---|---|---|---|
| ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ |
| 125.03 | 5.06 | 114.11 | 1.95 | 151.96 | 0.63 | 38.35 | 18.68 |
| 239.29 | 6.49 | 190.52 | 8.27 | 152.17 | 6.00 | 151.48 | 5.06 |
| 294.78 | 1.48 | 270.04 | 2.02 | 275.05 | 7.86 | 178.18 | 0.08 |
| 316.22 | 7.00 | 281.15 | 0.05 | 310.91 | 4.28 | 300.80 | 0.64 |
| 492.88 | 5.83 | 495.81 | 10.16 | 386.25 | 0.08 | 388.84 | 1.60 |
| 638.57 | 4.53 | 621.94 | 16.74 | 442.20 | 1.70 | 442.71 | 1.61 |
| 706.79 | 22.14 | 706.16 | 40.57 | 789.96 | 25.09 | 805.48 | 0.18 |
| 708.31 | 39.22 | 736.22 | 10.25 | 804.08 | 0.36 | 830.71 | 30.31 |
| 916.94 | 0.37 | 904.88 | 0.05 | 923.07 | 49.38 | 919.50 | 50.64 |
| 940.40 | 1.37 | 962.61 | 1.54 | 936.54 | 40.99 | 926.41 | 30.39 |
| 1003.99 | 28.52 | 992.86 | 31.23 | 1048.32 | 6.23 | 1051.98 | 8.89 |
| 1222.97 | 4.34 | 1210.17 | 0.28 | 1260.48 | 2.49 | 1237.49 | 6.34 |
| 1356.64 | 11.66 | 1346.45 | 21.92 | 1308.90 | 7.22 | 1313.38 | 5.65 |
| 1599.32 | 18.89 | 1607.30 | 24.50 | 1613.62 | 18.36 | 1616.02 | 27.98 |
| 2115.16 | 120.35 | 2116.78 | 143.03 | 2119.51 | 153.27 | 2120.23 | 150.45 |
| 2579.92 | 0.91 | 2604.15 | 0.30 | 2581.29 | 1.02 | 2619.49 | 1.65 |
| 3063.15 | 6.73 | 3066.88 | 7.92 | 3052.38 | 7.67 | 3050.93 | 7.05 |
| 3079.51 | 0.26 | 3089.06 | 0.40 | 3061.63 | 4.91 | 3074.23 | 3.52 |

[a]Calculated wavenumbers at the DFT/UB3LYP/aug-cc-pVTZ level. Scaling factors of 0.96, 0.97 and 0.98 are applied to the regions over 2800 $cm^{-1}$, between 2800 to 1900 $cm^{-1}$ and below 1900 $cm^{-1}$, respectively.

***Table S3.*** *Calculated wavenumbers and IR intensities of 2-isocyanoethenethial (**3**) and 2-isocyanothiirane (**4**).*[a]

| *syn*-**3** | | *anti*-**3** | | **4** | |
|---|---|---|---|---|---|
| ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ |
| 120.17 | 1.51 | 55.64 | 10.45 | 170.66 | 2.99 |
| 155.43 | 0.97 | 155.96 | 5.61 | 189.27 | 1.83 |
| 264.24 | 1.40 | 257.86 | 0.51 | 396.05 | 0.63 |
| 277.14 | 0.03 | 333.36 | 5.39 | 478.11 | 3.45 |
| 624.94 | 11.29 | 429.69 | 3.82 | 625.79 | 36.69 |
| 704.46 | 6.86 | 704.37 | 9.10 | 650.32 | 8.04 |
| 782.45 | 5.14 | 942.31 | 21.53 | 840.54 | 9.29 |
| 971.92 | 12.03 | 947.40 | 13.08 | 904.42 | 3.69 |
| 992.26 | 10.07 | 1000.71 | 7.61 | 977.62 | 18.05 |
| 1134.31 | 34.02 | 1117.97 | 41.76 | 1057.71 | 9.79 |
| 1244.13 | 0.05 | 1229.34 | 0.45 | 1115.54 | 6.17 |
| 1297.50 | 19.22 | 1287.05 | 48.45 | 1145.62 | 5.04 |
| 1375.91 | 33.13 | 1367.88 | 10.06 | 1347.44 | 26.36 |
| 1425.35 | 19.98 | 1430.69 | 13.63 | 1448.08 | 5.24 |
| 2163.30 | 174.52 | 2155.71 | 183.63 | 2138.63 | 207.04 |
| 2889.29 | 9.08 | 2899.58 | 7.42 | 3001.58 | 6.75 |
| 2911.53 | 0.41 | 2967.12 | 2.19 | 3039.63 | 0.62 |
| 2952.58 | 21.60 | 2976.14 | 4.85 | 3089.36 | 0.42 |

[a]Calculated wavenumbers at the DFT/UB3LYP/aug-cc-pVTZ level. Scaling factors of 0.96, 0.97 and 0.98 are applied to the regions over 2800 $cm^{-1}$, between 2800 to 1900 $cm^{-1}$ and below 1900 $cm^{-1}$, respectively.

***Table S4.*** *Calculated wavenumbers and IR intensities of Dewar thiazole and 2-cyanothiirane.*[a]

| Dewar thiazole | | 2-cyanothiirane | |
|---|---|---|---|
| ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ |
| 366.75 | 0.23 | 177.34 | 4.99 |
| 398.29 | 5.36 | 217.09 | 4.60 |
| 594.24 | 17.38 | 465.65 | 2.71 |
| 695.27 | 15.21 | 540.09 | 2.94 |
| 784.81 | 17.65 | 629.25 | 22.46 |
| 841.54 | 8.19 | 660.94 | 0.12 |
| 887.00 | 10.15 | 836.91 | 0.83 |
| 903.03 | 14.61 | 907.15 | 2.31 |
| 943.13 | 0.60 | 967.80 | 6.17 |
| 994.24 | 16.81 | 1064.79 | 10.38 |
| 1062.44 | 7.95 | 1102.30 | 2.84 |
| 1143.88 | 1.51 | 1125.40 | 0.94 |
| 1211.64 | 15.31 | 1331.12 | 2.96 |
| 1262.75 | 18.90 | 1452.11 | 1.72 |
| 1569.77 | 10.49 | 2276.07 | 12.52 |
| 3037.81 | 14.72 | 3005.01 | 6.31 |
| 3070.13 | 4.12 | 3031.65 | 0.89 |
| 3088.59 | 0.29 | 3092.38 | 0.24 |

[a]Calculated wavenumbers at the DFT/UB3LYP/aug-cc-pVTZ level. Scaling factors of 0.96, 0.97 and 0.98 are applied to the regions over 2800 $cm^{-1}$, between 2800 to 1900 $cm^{-1}$ and below 1900 $cm^{-1}$, respectively.

***Table S5.*** *Calculated wavenumbers and IR intensities of (methyleneamino)-ethenethione (**5**) and N-ethynylthiformamide (**6**).*[a]

| *anti*-**5** | | *syn*-**5** | | *syn*-**6** | | *anti*-**6** | |
|---|---|---|---|---|---|---|---|
| ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ | ν / $cm^{-1}$ | Intensity / km $mol^{-1}$ |
| 125.13 | 9.95 | 76.87 | 16.54 | 134.99 | 2.04 | 115.14 | 0.22 |
| 143.29 | 0.65 | 130.29 | 4.95 | 244.60 | 8.69 | 157.83 | 0.86 |
| 397.98 | 2.39 | 385.59 | 5.45 | 330.97 | 3.40 | 369.62 | 10.21 |
| 407.39 | 5.27 | 408.49 | 12.48 | 475.37 | 0.21 | 439.97 | 0.44 |
| 529.74 | 8.10 | 586.44 | 15.93 | 503.98 | 95.26 | 509.95 | 10.58 |
| 626.13 | 10.47 | 645.11 | 13.33 | 561.09 | 46.26 | 534.14 | 66.21 |
| 802.18 | 3.39 | 776.42 | 10.62 | 687.23 | 0.07 | 630.52 | 49.33 |
| 867.08 | 29.33 | 847.27 | 13.11 | 702.97 | 53.06 | 709.65 | 34.24 |
| 994.76 | 26.04 | 1008.95 | 22.39 | 860.49 | 0.70 | 914.03 | 31.93 |
| 1060.81 | 4.55 | 1030.66 | 8.70 | 886.38 | 7.57 | 1003.16 | 28.59 |
| 1196.66 | 33.45 | 1187.26 | 2.40 | 1042.22 | 38.50 | 1055.57 | 38.14 |
| 1276.71 | 63.96 | 1285.26 | 3.01 | 1255.41 | 183.08 | 1247.80 | 350.47 |
| 1457.13 | 4.79 | 1459.43 | 19.06 | 1389.64 | 236.67 | 1309.07 | 14.74 |
| 1625.56 | 28.18 | 1635.90 | 55.39 | 1485.56 | 24.82 | 1496.68 | 305.83 |
| 1761.49 | 432.96 | 1725.47 | 341.90 | 2178.52 | 45.64 | 2173.79 | 126.15 |
| 2891.02 | 47.76 | 2905.39 | 25.40 | 2976.37 | 24.06 | 2994.90 | 4.22 |
| 2933.81 | 16.90 | 3028.66 | 13.77 | 3335.53 | 100.07 | 3332.53 | 138.78 |
| 3035.73 | 11.89 | 3033.36 | 7.93 | 3418.55 | 57.86 | 3389.01 | 44.40 |

[a]Calculated wavenumbers at the DFT/UB3LYP/aug-cc-pVTZ level. Scaling factors of 0.96, 0.97 and 0.98 are applied to the regions over 2800 $cm^{-1}$, between 2800 to 1900 $cm^{-1}$ and below 1900 $cm^{-1}$, respectively.

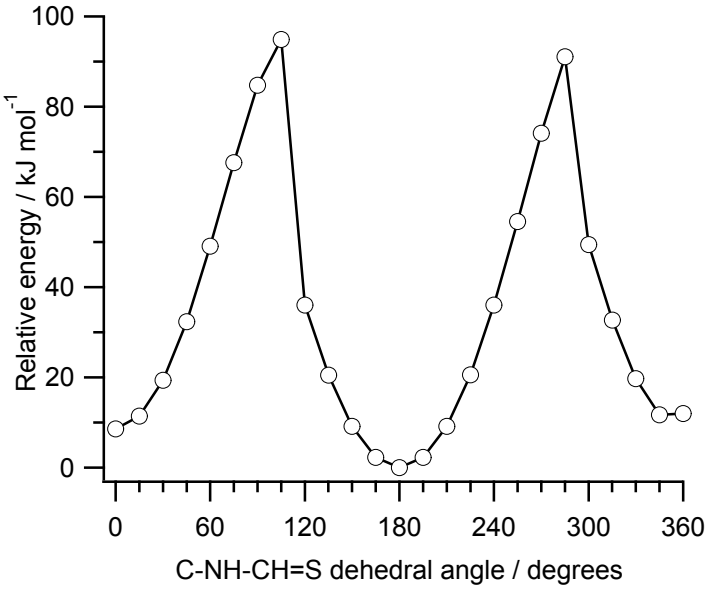


***Fig. S1.*** *Calculated potential energy around the C−NH−CH=S dihedral angle of N-ethynylthioformamide (**6**) at the DFT/UB3LYP/aug-cc-pVTZ level by one-step optimization at an interval of 15°.*